Review of the AFWO Klamath River Grab Sample Water Quality Database

March 9, 2005

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1.0 Introduction

The Arcata Office (AFWO) of the U.S. Fish and Wildlife Service (USFWS) has been collecting water quality data in the Klamath River since 2001. Since that time a significant part of the program has included the operation of Hydrolab DataSondes that collected information on water temperature, dissolved oxygen, pH, and specific conductance at approximately 12 sites below Iron Gate Dam in the mainstem Klamath River and major tributaries. In addition to operating sondes, AFWO also collected nutrient grab samples (and Chlorophyll a) at many of the same locations as the sondes at 2 to 4 week intervals from May through October. On occasion additional grab samples were collected for special studies that included diurnal evaluations of nutrients, effects of a pulse flow on re-suspension of nutrient matter in the water column, and an evaluation of fall turnover of Iron Gate Reservoir on downstream river water quality. In 2004 some fecal/total coliform information was also collected at various sites. To date, approximately 10,000 water samples have been analyzed and the results stored in a MS Access database.

To date the AFWO staff has not been able to fully evaluate all aspects of the Water Quality Monitoring Program. In particular, the grab sample database that has been accumulated over the period of four years has not undergone a comprehensive and critical review. This report focuses on the quality of the water quality database, the data sampling protocol, and the use of the data in the database rather than an analysis and interpretation of the data.

The primary objective of this review is to assess the data quality prior to its release to other agencies engaged in the study of the Klamath River basin. This review will also assist the contractors in their own analysis of the data, and in formulating recommendations for future sampling in the Klamath River.

2.0 Data Review

The analysis of any water quality database is typically focused on: the density of the spatial and temporal coverage of the waterbody or watershed of concern; the constituents for which data are available and whether they can be used to address the water quality problem of interest; the quality of the data, meaning their reliability and representativeness of the water quality actually present; and the ease with which the data may be retrieved from the database. Those who use the water quality data from the database must assess whether the spatial and temporal coverage and the constituents available meet their needs, i.e., whether their planned use of the data mesh with the purpose for which the data were gathered. What any user does expect is ease of data access and reliability of the data and adequate information in the database to judge that reliability, and it is these characteristics which were analyzed for in the AFWO grab sample database.

To help the user of the AFWO grab sample database make use of the data therein, this review will focus first on the database itself and the ease of access of data from it, on sample collection, sample handling, sample storage, the analytical methods used in analysis, and then on QA/QC protocols and what that information says about the quality of the grab sample data. Then some attention will be given to using the database. Following are the steps taken in the analysis of the AFWO grab sample database:

- Because the AFWO grab sample database is housed on the Microsoft relational database program Access, an analysis of how the database takes advantage of the features of Access was addressed first to judge the ease of access of data;
- Then the content of the various tables that have been populated with grab sample data and related information were examined for the completeness and robustness of the data and the associated information needed to judge the quality of the data;
- Because the quality of the grab sample data contained in the database is of greatest interest to those who wish to use it, the next step was to examine:
  - Sampling and sample handling protocols employed, the analytical methods used to determine constituent concentrations, and the QA/QC performed by the laboratories performing analyses;
  - Sample handling times were checked against times recommended by regulatory agencies, analytical accuracy and precision were checked using spikes and duplicates data, and sample contamination by sampling and analytical procedures were assessed using blanks data.
- Finally, some recommendations and cautions to those who use the system were developed.

3.0 Grab Sample Database

The AFWO grab sample database is stored in the Microsoft Access database, a user-friendly relational database system introduced in 1992. It has the capability of interfacing with other popular PC database programs like dBASE, Paradox, and MS FoxPro and many SQL databases on servers, minicomputers, and mainframes (Viescas 1997).

As implemented in Access at this time, the AFWO grab sample database employs the most basic features of Access, namely the table feature, which makes the database easily accessible to other users and unencumbered by queries, forms, etc. Users are able to develop their own queries to meet their needs. The grab sample database consists of four tables. The main main table contains all of the grab sample data from 2001 through 2004 in a single file named "tblGrabResults2001to2004" (with 10,164 records). A second table, also with 10,164 records, named "tblGrabResultsWithAudit2001to2004" gives sample results with water quality data such as temperature, pH, specific conductivity, and dissolved oxygen at the time of sampling, data acquired using the Hydrolab Quanta multiprobe instrument. A third table, "tblSites" with 102 records lists the sampling sites and related information, and the fourth table, "tblDischarge" (14,640 records) contains river discharge estimates at nine stations on the Klamath River mainstem and tributaries with fixed gaging instruments. These tables, their contents, and descriptions of the contents of their fields are described in more detail in Turner (2005).

The 51 sampling stations from which grab samples were taken are given in alphabetical order in Table 3.1 and by River Mile (descending from highest to lowest or up the basin to down the basin) in Table 3.2. Grab samples were not taken at all of the stations listed in the tblSites database, so the user should not expect to find records for some of the stations listed therein. The number of grab samples taken at each station is given in Table 3.3. Clearly the majority of grab samples were taken in the Klamath River mainstem below Iron Gate Dam with fewer samples taken in the mainstem Klamath River above Iron Gate Dam and in the tributaries such as the Salmon, Scott, Shasta, and Trinity Rivers.

The grab sample database includes the following constituents: measures of inorganic constituents - Alkalinity, Calcium, Magnesium, Total Suspended Solids, and Total Dissolved Solids; carbonaceous organic material represented by Biochemical Oxygen Demand and Total Organic Carbon; nutrient forms, namely nitrogen (Total Kjeldahl Nitrogen or TKN, Ammonia-N, Nitrite-N, Nitrate-N) and phosphorus (Total P and Ortho-P); bacteria represented by the Total Coliform and Fecal Coliform groups; and algal forms represented by Chlorophyll a and Pheophytin. Thus, the key constituents needed to understand the basic limnology of the river and the impact of waste discharges, runoff, impoundment, and so forth on the organics, nutrients, and vegetation in the river are being gathered.

The names used for these constituents in the Analyte field of the main database are as follows:

Alkalinity
Ammonia Nitrogen

Biochemical Oxygen Demand
Calcium
Chlorophyll a
Fecal Coliform
Magnesium
Nitrate (as Nitrogen)
Nitrite (as Nitrogen)
Nitrogen- Total Kjeldahl
Non-Filterable Residue(TSS)
Organic Nitrogen-N
Orthophosphate Phosphorus
Pheophytin
Total Coliform
Total Dissolved Solids
Total Organic Carbon
Total Phosphate Phosphorus

These names as given above or some portion (using the search features of Access) are needed to retrieve data from the database. Later in this report, Biochemical Oxygen Demand may be represented as BOD, Total Kjeldahl Nitrogen as TKN, Total Dissolved Solids as TDS, and Total Organic Carbon as TOC.

Data desired in a water quality database include sampling station, sampling date (and time), analyte, results of analyses, and measures of data quality. For the grab samples, the main database "tblGrabResults2001to2004" has this information for each of the 10,164 records. There are occasional records for which sampling time is missing, but sampling date is always entered. On the whole, the main database "tblGrabResults2001to2004" has the key "what", "where", and "when" information and is fully useable in this regard.

Other data desirable in a water quality database include further data related to sampling that will link the data to field notes, other projects, etc., laboratory analysis data such as:

- date of analysis,
- methods used to determine the analyte concentration, MDL and RDL values for those methods, and information to link results to laboratory records,
- the laboratory or laboratories performing analyses,
- and QA/QC data such as blanks, duplicates, and spikes.

The main database "tblGrabResults2001to2004" has only some of these data at this point, and it appears that much of the information needed will have to come from laboratory report sheets. Thus, some of the "how" information is missing at this point.

The same is true of the "tblGrabResultsWithAudit2001to2004" table. In this database, there are a significant number of sampling days for which Hydrolab Quanta data are not available. AFWO has rightfully omitted such data when equipment malfunctioned or the data were found to be erroneous because of poor or missing calibrations. On occasion, these measurements were not collected.

The table containing U.S. Geological Survey discharge data, "tblDischarge", is remarkably complete and of course permits the grab sample database user to relate water quality results to discharges. Out of the 14,640 records in the file, discharge data are given for all but 21 records.

For the SA site, discharge data listed for October 2004 through December 2004 are listed as Provisional as is typical of USGS before final release of their data. Once these data are finalized, it is anticipated that the tblDischarge database will be updated. Other stations include data only through early October 2004 (see Table 3.4). Average, maximum, and minimum flows for the time period provided are also given in this table.

The "who" information relates to the laboratories performing analyses on the grab samples collected. Seven names of laboratories are included in the database. In alphabetical order they are: Aquatic Research, Inc.; E.S. Babcock and Sons; ETS; NCL; Sequoia Analytical; Sierra Environmental Monitoring; and Sierra Foothill. These laboratories analyzed for different constituents in the grab samples over certain periods during the four years samples were gathered. These laboratories and the analyses and years they were performed are given below:

Aquatic Research, Inc.
Seattle, WA
Ammonia N in 2004

E.S. Babcock and Sons, Inc.
Riverside, CA
http://www.babcocklabs.com/
TOC in July, August, and September 2001

ETS Laboratories, Inc.
Petaluma, CA
Chlorophyll a and Pheophytin all years

North Coast Laboratories LTD.
Arcata, CA
http://www.northcoastlabs.com/
Alkalinity, Calcium, Magnesium, TDS, TSS, BOD, TOC, nitrogen forms (TKN, Ammonia N, Nitrite N, Nitrate N), phosphorus forms (Total P and Ortho P), bacteria (Total Coli and Fecal Coli) from 2001 through 2004

Sequoia Analytical Company
Riverside, CA
http://www.sequoialabs.com/
TKN 2004

Sierra Environmental Monitoring, Inc.
Reno, NV
http://www.sem-analytical.com/
Nitrogen forms 2001 to 2003

Sierra Foothill Laboratory
Jackson, CA
http://www.sierrafoothilllab.com/Default.htm
Total Organic Carbon 2001 through 2003

The analytical methods used by the laboratories are not provided at this time. However, this is information that can be obtained from the laboratories. However, the MDL and RDL values often are given, which provide some indication of the methods used. More importantly, they indicate the sensitivity of the methods used.

Some laboratories changed methods and/or changed sensitivity of their methods over time, and these changes are reflected in the database. It is up to the user to track these changes in interpreting the data from the database.

Several laboratories were used over this four year period as noted above and there was some overlap of constituent analysis. Normally, intra-laboratory comparisons to discern basic differences in methodology and operation among the laboratories for each analyte are performed, and there is one analysis of Chlorophyll a for which a laboratory comparison was performed. The user will need to consider this in examining temporal trends of the data.

Finally, turbidity data have been collected in the Klamath River and its tributaries from 2001 through 2004 using a LaMotte 2020 turbidimeter. The sampling procedures are given in Turner (2005), and some 448 turbidity values are available. This database will be added to the grab sample database by AFWO in the near future.

Table 3.1. AFWO grab sample stations in the Klamath River Basin (sorted alphabetically)

Site	Site Description	First Order RM	Second Order RM	Third Order RM	Elevation	Latitude	Longitude
BC	Bogus Creek	189.6	0.2			41 55 46	122 26 30
BL	Bluff Creek @ mouth	49.5	0.1		320	41 14 25.6	123 39 11
BVC	Beaver Creek	161.1	0.1			41 52 15	122 48 57
C1	Klamath River above Copco 1	205.5			2530	41 57 57.3	122 12 57.9
C2	Klamath River below Copco 2	196.5			2130	41 58 23.7	122 21 48.9
CLR	Clear Creek	98.6	0.1		960	41 42 35.5	123 26 55.8
DLN	Dillon Creek	84.2	0.1		780	41 34 32	123 32 18
ELK	Elk Creek	105.5	0.1		1040	41 46 49.1	123 23 34.7
EM	Klamath River Estuary Mainstem	0.1			40	41 32 37	124 04 44
GOF	Klamath River below Fort Goff, River access point 66, Seattle Creek	121.4				41 50 37	123 18 02
GOT	Klamath River below Gottville	164.9				41 51 30	122 45 03
HAM	Klamath River below Hamburg, Access pt 56 (Rodney Pt.)	140				41 48 58	123 07 35
HC	Klamath River below Happy Camp	100.8			960	41 43 47	123 25 28
IG	Klamath River at Iron Gate Hatchery Bridge	189.8			2178	41 55 53	122 26 24
IGRB	Iron Gate Reservoir Bottom	190.1				41 56 20	122 25 53
IGRS	Iron Gate Reservoir Surface	190.1				41 56 20	122 25 53
JB	Klamath River before JC Boyle Powerhouse (Bypass)	220.5			3350	42 05 37	122 04 09
JC	Klamath River below JC Boyle return	217			3340	42 03 12.5	122 05 20.8
JP	Klamath River at JC Boyle Powerhouse	220.4			3340	42 05 35	122 04 15
K1	Klamath River above Shasta	176.8			1860	41 49 52	122 35 31
K2	Klamath River above the Scott River (small pullout across from green highway sign- Horse Creek 4 miles)	143.2			1520	41 46 45.7	123 01 59.2
KBC	Klamath River above Blue Creek	16.5			40	41 25 24	123 55 40
KD	Klamath River above Dillon Creek	84.3			780	41 34 37	123 32 21
KELK	Klamath River 200 yards below Elk Creek, above Waste Water Treatment Plant	105.4				41 46 45	123 23 38
KN	Klamath River below Keno Dam	223.2			4095	42 08 03	121 56 50
KRSL	Klamath River at Stateline	209.2				42 00 26	122 11 15
KS	Klamath Straights Drain	240.5			4094.1	42 04 52	121 50 34

KSA	Klamath River above Salmon River	66.1			455	41 22 39.7	123 29 40.8
L1	Little Shasta River CDFG wildlife area	176.6	15.7	11.8	2400	41 42 25	122 26 12
L2	Little Shasta River	176.6	15.7	6.5	2100	41 43 23	122 22 06
LR	Link River below dam	253.2			4094.1	42 12 05	121 47 17
MF	Klamath River at Martins Ferry	40.4			160	41 12 26	123 45 19
OR	Klamath River at Orleans	59.1			400	41 18 12	123 32 00
RB	Klamath River at Round Bar pool, near town of Klamath River	158.5				41 51 3.6	122 50 7.9
RCC	Red Cap Creek, 150' upstream of Allen Bridge	52.7	0.3			41 15 34	123 36 01
S1	Shasta River at Louie Rd Crossing	176.6	32		2300	41 35 27	122 26 13
S2	Shasta River at A12 Bridge	176.6	22.6		2250	41 38 54	122 29 54
S3	Shasta River at Montague Grenada	176.6	15.1		2160	41 42 33	122 32 14
S4	Shasta River above Yreka Creek	176.6	7.9		2100	41 46 21	122 35 31
SA	Salmon River near mouth	66	1.01		480	41 22 36	123 28 33
SC	Scott River near mouth	143	1.5		1600	41 45 57	123 01 16
SH	Shasta River near mouth	176.6	0.5		2031	41 49 30	122 35 33
SRWC	Shasta River above Willow Creek (near rt 3)	176.6				41 43 35	122 33 31
SV	Klamath River at Seiad Valley	128.5			1320	41 51 15	123 13 49
TC	Klamath River above Tully Cr. (below MF)	38.5			280	41 13 41	123 46 20
TG	Klamath River at Terwer	6.7			8	41 30 55	123 59 56
TR	Trinity River near mouth	43.5	0.5		240	41 10 54	123 42 14
UL	Ullathorne Creek (Below Orleans)	56.1	0.1			41 17 30	123 34 10
WE	Klamath River at Weitchepec	43.6			240	41 11 09	123 42 03
Y2	Yreka Creek above Waste Water Plant	176.6	7.6			41 44 24	122 37 47
YR	Yreka Creek	176.6	7.6	0.6	2000	41 46 21	122 36 14

Table 3.2. AFWO grab sample stations in the Klamath River Basin (sorted by River Mile)

Site	Site Description	First Order RM	Second Order RM	Third Order RM	Elevation	Latitude	Longitude
LR	Link River below dam	253.2			4094.1	42 12 05	121 47 17
KS	Klamath Straights Drain	240.5			4094.1	42 04 52	121 50 34
KN	Klamath River below Keno Dam	223.2			4095	42 08 03	121 56 50
JB	Klamath River before JC Boyle Powerhouse (Bypass)	220.5			3350	42 05 37	122 04 09
JP	Klamath River at JC Boyle Powerhouse	220.4			3340	42 05 35	122 04 15
JC	Klamath River below JC Boyle return	217			3340	42 03 12.5	122 05 20.8
KRSL	Klamath River at Stateline	209.2				42 00 26	122 11 15
C1	Klamath River above Copco 1	205.5			2530	41 57 57.3	122 12 57.9
C2	Klamath River below Copco 2	196.5			2130	41 58 23.7	122 21 48.9
IGRB	Iron Gate Reservoir Bottom	190.1				41 56 20	122 25 53
IGRS	Iron Gate Reservoir Surface	190.1				41 56 20	122 25 53
IG	Klamath River at Iron Gate Hatchery Bridge	189.8			2178	41 55 53	122 26 24
BC	Bogus Creek	189.6	0.2			41 55 46	122 26 30
K1	Klamath River above Shasta	176.8			1860	41 49 52	122 35 31
S1	Shasta River at Louie Rd Crossing	176.6	32		2300	41 35 27	122 26 13
S2	Shasta River at A12 Bridge	176.6	22.6		2250	41 38 54	122 29 54
L1	Little Shasta River CDFG wildlife area	176.6	15.7	11.8	2400	41 42 25	122 26 12
L2	Little Shasta River	176.6	15.7	6.5	2100	41 43 23	122 22 06
S3	Shasta River at Montague Grenada	176.6	15.1		2160	41 42 33	122 32 14
S4	Shasta River above Yreka Creek	176.6	7.9		2100	41 46 21	122 35 31
YR	Yreka Creek	176.6	7.6	0.6	2000	41 46 21	122 36 14
Y2	Yreka Creek above Waste Water Plant	176.6	7.6			41 44 24	122 37 47
SH	Shasta River near mouth	176.6	0.5		2031	41 49 30	122 35 33
SRWC	Shasta River above Willow Creek (near rt 3)	176.6				41 43 35	122 33 31
GOT	Klamath River below Gottville	164.9				41 51 30	122 45 03
BVC	Beaver Creek	161.1	0.1			41 52 15	122 48 57
RB	Klamath River at Round Bar pool, near town of Klamath River	158.5				41 51 3.6	122 50 7.9
K2	Klamath River above the Scott River (small pullout across from green highway sign- Horse Creek 4 miles)	143.2			1520	41 46 45.7	123 01 59.2
SC	Scott River near mouth	143	1.5		1600	41 45 57	123 01 16

HAM	Klamath River below Hamburg, Access pt 56 (Rodney Pt.)	140			41 48 58	123 07 35
SV	Klamath River at Seiad Valley	128.5		1320	41 51 15	123 13 49
GOF	Klamath River below Fort Goff, River access point 66, Seattle Creek	121.4			41 50 37	123 18 02
ELK	Elk Creek	105.5	0.1	1040	41 46 49.1	123 23 34.7
KELK	Klamath River 200 yards below Elk Creek, above Waste Water Treatment Plant	105.4			41 46 45	123 23 38
HC	Klamath River below Happy Camp	100.8		960	41 43 47	123 25 28
CLR	Clear Creek	98.6	0.1	960	41 42 35.5	123 26 55.8
KD	Klamath River above Dillon Creek	84.3		780	41 34 37	123 32 21
DLN	Dillon Creek	84.2	0.1	780	41 34 32	123 32 18
KSA	Klamath River above Salmon River	66.1		455	41 22 39.7	123 29 40.8
SA	Salmon River near mouth	66	1.01	480	41 22 36	123 28 33
OR	Klamath River at Orleans	59.1		400	41 18 12	123 32 00
UL	Ullathorne Creek (Below Orleans)	56.1	0.1		41 17 30	123 34 10
RCC	Red Cap Creek, 150' upstream of Allen Bridge	52.7	0.3		41 15 34	123 36 01
BL	Bluff Creek @ mouth	49.5	0.1	320	41 14 25.6	123 39 11
WE	Klamath River at Weitchepec	43.6		240	41 11 09	123 42 03
TR	Trinity River near mouth	43.5	0.5	240	41 10 54	123 42 14
MF	Klamath River at Martins Ferry	40.4		160	41 12 26	123 45 19
TC	Klamath River above Tully Cr. (below MF)	38.5		280	41 13 41	123 46 20
KBC	Klamath River above Blue Creek	16.5		40	41 25 24	123 55 40
TG	Klamath River at Terwer	6.7		8	41 30 55	123 59 56
EM	Klamath River Estuary Mainstem	0.1		40	41 32 37	124 04 44

Table 3.3. Number of grab samples taken at stations in the Klamath River Basin

Site	Site Description	River Mile	Number of Grab Samples Taken
LR	Link River below dam	253.2	200
KS	Klamath Straights Drain	240.5	134
KN	Klamath River below Keno Dam	223.2	167
JB	Klamath River before JC Boyle Powerhouse (Bypass)	220.5	132
JP	Klamath River at JC Boyle Powerhouse	220.4	136
JC	Klamath River below JC Boyle return	217	160
KRSL	Klamath River at Stateline	209.2	16
C1	Klamath River above Copco 1	205.5	137
C2	Klamath River below Copco 2	196.5	205
IGRB	Iron Gate Reservoir Bottom	190.1	36
IGRS	Iron Gate Reservoir Surface	190.1	37
IG	Klamath River at Iron Gate Hatchery Bridge	189.8	1245
BC	Bogus Creek	189.2	15
K1	Klamath River above Shasta	176.8	170
L1	Little Shasta River CDFG wildlife area	176.6	30
L2	Little Shasta River	176.6	28
S1	Shasta River at Louie Rd Crossing	176.6	96
S2	Shasta River at A12 Bridge	176.6	73
S3	Shasta River at Montague Grenada	176.6	79
S4	Shasta River above Yreka Creek	176.6	81
SH	Shasta River near mouth	176.6	920
SRWC	Shasta River above Willow Creek (near rt 3)	176.6	15
Y2	Yreka Creek above Waste Water Plant	176.6	14
YR	Yreka Creek	176.6	81
GOT	Klamath River below Gottville	164.9	15
BVC	Beaver Creek	161.1	15
RB	Klamath River at Round Bar pool, near town of Klamath River	158.5	44
K2	Klamath River above the Scott River (small pullout across from green highway sign- Horse Creek 4 miles)	143.2	205
SC	Scott River near mouth	143	612
HAM	Klamath River below Hamburg, Access pt 56 (Rodney Pt.)	140	15
SV	Klamath River at Seiad Valley	128.5	656
GOF	Klamath River below Fort Goff, River access point 66, Seattle Creek	121.4	15
ELK	Elk Creek	105.5	15
KELK	Klamath River 200 yards below Elk Creek, above Waste Water Treatment Plant	105.4	15
HC	Klamath River below Happy Camp	100.8	544
CLR	Clear Creek	98.6	15
KD	Klamath River above Dillon Creek	84.3	14
DLN	Dillon Creek	84.2	15
KSA	Klamath River above Salmon River	66.1	39
SA	Salmon River near mouth	66	504
OR	Klamath River at Orleans	59.1	701

UL	Ullathorne Creek (Below Orleans)	56.1	15
RCC	Red Cap Creek, 150' upstream of Allen Bridge	52.7	15
BL	Bluff Creek @ mouth	49.5	12
WE	Klamath River at Weitchepec	43.6	420
TR	Trinity River near mouth	43.5	628
MF	Klamath River at Martins Ferry	40.4	446
TC	Klamath River above Tully Cr. (below MF)	38.5	155
KBC	Klamath River above Blue Creek	16.5	26
TG	Klamath River at Terwer	6.7	699
EM	Klamath River Estuary Mainstem	0.1	102

Table 3.4. Discharge statistics at selected gaged sites in the Klamath River Basin

Site	**River Mile**	**Count Of Date**	**Count Of Discharge (cfs)**	**Avg Of Discharge (cfs)**	**Max Of Discharge (cfs)**	**Min Of Discharge (cfs)**	**Maximum Date**	**Minimum Date**
JCB*	217	730	711	1,176.6	3,850	355	2/24/2004	2/25/2002
IG*	189.8	1436	1436	1,342.6	4,180	614	12/7/2004	1/1/2001
SH	176.6	1437	1435	143.6	1,500	10	11/15/2004	1/1/2001
IG+SH*	176.5	1391	1391	1,498.8	5,054	630	10/22/2004	1/1/2001
SC	143	1391	1391	478.7	7,330	3	10/22/2004	1/1/2001
SV*	128.5	1230	1230	2,593.5	16,400	678	10/22/2004	1/1/2001
SA	66	1461	1461	1,471.4	17,100	60	12/31/2004	1/1/2001
OR*	59.1	1391	1391	6,339.3	56,000	1,190	10/22/2004	1/1/2001
HPA	43.5	1391	1391	4,426.8	62,200	499	10/22/2004	1/1/2001
OR+HPA*	43.4	1391	1391	10,767.5	118,200	1,790	10/22/2004	1/1/2001
TG*	6.7	1391	1391	13,878.9	174,000	1,890	10/22/2004	1/1/2001

* Klamath River stations
Note that the JCB site is the same as JC

4.0 Sampling and QA/QC

4.1 Collection, Handling, and Storage of Samples

The Protocol for Collection of Nutrients Grab Samples (2005) published by the AFWO describes the procedures used for collection of water samples from the Klamath River and its tributaries, how the samples were handled after collection, and how they were stored from the time of collection to delivery at the laboratory. The methods described in this Protocol indicates that standard field procedures were used that would protect the samples from contamination, deterioration, and mishandling.

Because some sampling date and analysis date information are provided in the grab sample database, it was possible to check sample handling times for a portion of the data, and the results are shown in Table 4.1. For the most part, the laboratories analyzed the samples for the various constituents within the prescribed holding times. Where exeedances are noted, the number of times the prescribed holding time was exceeded is relatively small. An exception is for BOD, and some of those exceedances may be for long-term BOD analyses. The exceedances for the nitrogen forms are relatively small; these samples are preserved at the time of sampling, so it is doubtful that much sample deterioration occurred in the short additional time the samples were held before analysis.

Given the sampling protocol and the holding time analysis, the user of the grab sample data should have confidence in the data as far as sampling is concerned.

4.2 QA/QC Protocols and Analytical Analyses

Definitions and Approach

For QA/QC purposes, it was desired to estimate the precision, accuracy, completeness, representativeness, and comparability of the data. Precision measures the reproducibility of the sampling and analytical methodology. Laboratory and field precision is defined as the relative percent difference (RPD) between duplicate sample analyses, while the laboratory duplicate samples measure the precision of the analytical method. Precision can be calculated as:

$$\text{Relative Percent Difference} = \frac{(M_1 - M_2)x100}{(M_1 + M_2)/2} \qquad (4\text{-}1)$$

where M_1 = measurement 1 and M_2 = measurement 2.

Accuracy is defined as the degree to which the analytical measurement reflects the true concentration of the constituent of interest in the sample and may be determined by the percent recovery of a known spike from the sample. The result is expressed as a percent of the spike recovered from the sample:

$$\text{Percent Recovery} = \frac{(SSR - SR)x100}{SA} \qquad (4\text{-}2)$$

where SSR= spiked sample result, SR = sample result, and SA = spike added.

To develop measures of Precision and Accuracy, duplicate and spike samples were taken as described in Turner (2005). Blank samples were also run to determine the contribution of constituent to the blank by the field and laboratory methodology. The number of blanks (B), duplicates (D), and spikes (S) by analyte are shown in Table 4.2. Between 5% and 10% of the samples analyzed were for blanks and duplicates each. For Calcium, Ammonia-N, Nitrate-N, Total P, and Ortho P, spikes were prepared, and again between 5% and 10% of the samples analyzed were for spikes. This percent range is normal for water quality sampling programs. Of note in Table 4.2 is the number of analyses for each constituent; the highest number of analyses is for TKN at 813 while the lowest is for Total Coliform at 90.

Sample filtration (the column labeled F in Table 4.2) was performed on some samples in 2001 and 2002, and Turner (2005) contains information about the purpose and scope of this program.

Important to this discussion are the method detection and reporting detection limits. The reported detection limit (RDL) is defined as the minimum concentration of a chemical constituent that can be reliably quantified, while the method detection limit (MDL) is defined as the minimum concentration of a chemical constituent that can be detected.

Blank Samples

Table 4.3 shows the results of the blanks indicating the extent of sample contamination by the field and laboratory methods. The total number of blanks analyzed as shown in this table matches the same number in Table 4.2, and of that total the number of non-detects (ND) and detects is also given. For example, for Alkalinity, there were 32 non-detects, i.e., no field or laboratory contamination was evident, and 20 detects, and the average concentration of Alkalinity in the detect samples was 1.78 mg/L, the maximum was 3.7 mg/L, and the minimum was 1 mg/L. What should be evident is the large proportion of non-detects for all of the analytes indicating that field and laboratory contamination was not occurring often. When it did occur, the concentrations appear small, and the usual way of determining whether these concentrations are of concern is to compare them to the RDL. If the values are greater than twice the RDL, then contamination may be of concern. As shown in Table 4.4, the number of blanks for each analyte with concentrations greater than twice the RDL is shown to be zero for over half the analytes. Those analytes with non-zero values have very few such high cases except for Pheophytin. Some 14 blanks for Pheophytin (see Table 4.3) contained measurable concentrations and of those, 10 had concentrations more than twice the RDL. The last column of Table 4.4 shows the highest ratio of the analyte concentration in the blank to the RDL. A high value of this ratio may raise questions about the usability of some analyte data. The only analyte that appears to be in this category is Pheophytin. Because the blanks and the RDL values are in the grab sample database, the user can easily calculate these ratio and judge which data they may wish to omit. In summary, the blanks data indicate very low contamination by field and laboratory methods.

Precision

Information about Precision of the sampling and analytical program was obtained from the duplicates that were run as part of the QA/QC program. Table 4.5 shows the results of the analysis of duplicates for which Precision was estimated by Equation 4-1 above, expressed as a percent, and the three statistics calculated. It is instructive to note the number of detects used to calculate these estimates shown in Table 4.5; for some analytes like Ammonia-N and Nitrite-N, there were very few estimates of Precision that could be calculated because of the many non-detects found for the duplicates. The Precision goals were taken from a State of California publication (2000) which gave the Precision goals for groups of analytes. Those goals along with the average, maximum, and minimum estimates of precision give us a measure of the Precision of the grab sample data. For all of the inorganic analytes, precision falls within the 10% goal except for TSS, and its value is not far above the goal. Organics fall well within the 30% goal. Nitrogen and phosphorus forms are within the 5% precision goal except for TKN and Total P. The analytical methods for both of these analytes include sample digestion, and good Precision is often difficult to achieve for them. Precision estimates for Total and Fecal Coliforms and for Chlorophyll a and Pheophytin are elevated, but the values are not that unusual, particularly at low concentrations. On the whole, these estimates of Precision for all analytes are quite good.

Accuracy

Accuracy is the difference between a measured value and the true or expected value, and it is determined by comparing a sample to a known value. In this grab sample database, spikes were taken to estimate accuracy. By determining the analyte concentrations in a sample and in that sample with a known spike, it is possible to estimate accuracy and to express it as the percent of the spike and the ambient concentration recovered in the spiked sample (see Equation 4-2). Both sample and spiked sample analyses have been performed (see Table 4.2 for the number of spikes) and the results are in the grab sample database. AFWO personnel are in the process of gathering the known spike data to add to the database so that Accuracy can be estimated. An example of the level of accuracy achieved by the North Coast Laboratory on samples processed in September 2004 are as follows. For Ammonia-N, an average of 105.4% recovery from 4 samples; Nitrate-N, 98.1% from 1 sample; Total P, 102.2% from 4 samples; Ortho P, 97.3% from 2 samples; and TOC, 97.5% from 3 samples. The California Board's (2000) accuracy requirement is at least 90% for nutrients and 70% for organics. These recovery statistics indicate excellent accuracy.

Completeness

Data completeness is defined as the percentage of useable data (i.e., usable data divided by the total possible data). While the data needed to estimate completeness for the entire program are not available (and would be very difficult to gather), the completeness of the grab sample database can be estimated and it is quite high. That is, if one estimates the results that might be questionable based on the analysis above, the usable data in this database are well above 90%, the completeness goal of the California State Board (2000).

Representativeness

Representativeness expresses the degree to which sample data accurately and precisely represent environmental conditions, and comparability is a measure of the confidence with which one data set can be compared to another. The data in the grab sample database has been acquired through field sampling and sample handling methods that are in accordance with standard practice. Laboratory analysis of the sample collected has been carried out by laboratories practicing acceptable QA/QC procedures. Where problems such as that for Pheophytin have occurred, they have been addressed quickly by AFWO. While intra-laboratory comparisons would have been highly desirable for those analytes being tested by more than one laboratory, the lack of them does not negate the excellent quality that is evident from the QA/QC analysis above.

Table 4.1. Average, maximum, and minimum holding times for grab samples

Analyte Group	Analyte	Max Holding Time	Ave Holding Time (d)	Max Holding Time (d)	Min Holding Time (d)	n	Over Guidelines
Inorganics	Alkalinity	14 d	6.6	14	0	165	
	Calcium	6 mo	6.8	14	2	395	
	Magnesium	6 mo	6.8	14	2	367	
	Total Dissolved Solids	7 d	5.3	10	1	199	3 >7d
	TSS	7 d	4.1	9	0	197	
Organics	BOD	48 hr	5.0	16	1	90	54 exceed. >5 d
	Total Organic Carbon	28 d	7.9	29	1	375	1 >28d
Nitrogen	Total Kjeldahl N	28 d	10.9	34	2	536	9 >28d
	Ammonia N	28 d	9.7	28	1	564	
	Organic-N						Relate to TKN and Ammonia-N
	Nitrite-N	48 hr	1.4	3	0	125	11 >2.5 d
	Nitrate-N	48 hr	1.3	4	0	222	16 >2.5 d
Phosphorus	Total P	28 d	10.8	47	1	544	1 >28d
	Ortho P	48 hr	0.9	2	0	225	
Bacteria	Total Coli	24 hr					No data
	Fecal Coli	24 hr					No data
Algae	Chlorophyll a	Filter ≤48 hr, freeze filter up to 21 d	3.1	4	2	14	
	Pheophytin	Filter ≤48 hr, freeze filter up to 21 d					No data

Table 4.2. Blank (B), duplicate (D), and spike (S) samples taken and processed from 2001 through 2004 for each analyte. Original (O) and filtered (F) samples are also indicated.

Analyte Group	Analyte	B	D	S	F	O	Total
Inorganics	Alkalinity	52	55	0	50	519	676
	Calcium	45	45	30	0	466	586
	Magnesium	45	45	0	0	466	556
	TDS	55	57	0	50	537	699
	TSS	57	59	0	50	545	711
Organics	BOD	13	10	0	0	100	123
	TOC	46	51	0	0	520	617
Nitrogen	TKN	59	55	0	131	568	813
	Ammonia-N	52	49	46	109	453	709
	Org-N	14	14	0	39	154	221
	Nitrite-N	51	49	0	60	488	648
	Nitrate-N	58	56	38	60	552	764
Phosphorus	Total P	59	55	31	60	552	757
	Ortho P	59	55	26	70	545	755
Bacteria	Total Coliform	9	10	0	0	71	90
	Fecal Coliform	9	10	0	0	73	92
Algae	Chlorophyll a	51	52	0	0	493	596
	Pheophytin	51	52	0	0	489	592

Table 4.3. Estimates of method contamination from blanks

Analyte Group	Analyte	Ave Conc.	Max Conc.	Min. Conc.	No. ND	No. Detects	Total No.
Inorganics	Alkalinity	1.78	3.7	1	32	20	52
	Calcium	65.8	76	56	35	10	45
	Magnesium	ND	0	0	45	0	45
	TDS	47.4	120	10	50	5	55
	TSS	0.15	0.20	0.10	8	6	14
Organics	BOD	ND	0	0	13	0	13
	TOC	0.38	1.00	0.21	41	5	46
Nitrogen	TKN	0.15	0.21	0.10	44	15	59
	Ammonia-N	0.12	0.20	0.06	40	11	51
	Org-N	ND	0	0	59	0	59
	Nitrite-N	ND	0	0	51	0	51
	Nitrate-N	0.08	0.09	0.07	52	6	58
Phosphorus	Total P	0.046	0.068	0.037	54	5	59
	Ortho P	ND	0	0	59	0	59
Bacteria	Total Coliform	2	2	2	8	1	9
	Fecal Coliform	ND	0	0	9	0	9
Algae	Chlorophyll a	0.40	0.50	0.30	43	8	51
	Pheophytin	1.11	3.60	0.10	37	14	51

Table 4.4 Blanks with concentrations greater than twice the RDL

Analyte Group	Analyte	Number of Blanks with ≥ 2x RDL	Highest Ratio of Blank to RDL
Inorganics	Alkalinity	6	3.7
	Calcium	0	
	Magnesium	0	
	TDS	3	12
	TSS	0	
Organics	BOD	0	
	TOC	1	5
Nitrogen	TKN	1	2.1
	Ammonia-N	0	
	Org-N	0	
	Nitrite-N	0	
	Nitrate-N	0	
Phosphorus	Total P	2	3.4
	Ortho P	0	
Bacteria	Total Coliform	0	
	Fecal Coliform	1	20
Algae	Chlorophyll a	2	5
	Pheophytin	10	36

Table 4.5 Estimates of precision from duplicates

Analyte Group	Analyte	Precision Goal*	Ave RPD	Max RPD	Min RPD	No. Detects
Inorganics	Alkalinity	10%	1.1%	11.3%	0.0%	53
	Calcium	10%	2.1%	17.2%	0.0%	45
	Magnesium	10%	1.5%	16.1%	0.0%	45
	TDS	10%	6.0%	105.6%	0.0%	56
	TSS	10%	15.9%	99.8%	0.0%	53
Organics	BOD	30%	7.3%	11.8%	2.8%	2
	TOC	30%	7.8%	41.4%	0.0%	51
Nitrogen	TKN	5%	18.7%	70.7%	0.0%	37
	Ammonia-N	5%	7.7%	7.7%	7.7%	1
	Org-N		8.9%	25.0%	0.0%	13
	Nitrite-N	5%	0.0%	0.0%	0.0%	1
	Nitrate-N	5%	2.7%	31.4%	0.0%	35
Phosphorus	Total P	5%	14.3%	94.1%	0.0%	54
	Ortho-P	5%	3.5%	26.7%	0.0%	48
Bacteria	Total Coliform	2 SD	61.8%	174.3%	0.0%	10
	Fecal Coliform	2 SD	47.4%	139.5%	0.0%	10
Algae	Chlorophyll a		47.7%	124.8%	0.0%	44
	Pheophytin		67.6%	175.5%	0.0%	44

SD = Standard Deviation, and the Precision goal is 2 standard deviations from the long-term average for the laboratory
RPD = Relative Percent Difference
* Based on California State Water Resources Control Board (2000)

5.0 Conclusions

Based on this analysis of the AFWO grab sample database, the following conclusions were reached:

1. The AFWO grab sample database is easily usable in its Microsoft Access format, the database structure is described in a document authored by AFWO personnel, and the experienced Access user can easily construct queries to extract water quality data from it.
2. Water quality sampling has taken place from 2001 through 2004 at a number of locations in the Klamath River basin both in the river mainstem and the major tributaries and analyzed for inorganic, organic, nutrient, bacterial, and algal constituents, and the results from that sampling effort have been stored in the grab sample database along with associated laboratory and QA/QC information.
3. An analysis was made of the field sampling and sample handling protocols, and it was ascertained that standard practices were being used to gather and store samples prior to their delivery to a laboratory for analysis.
4. The water quality data in the grab sample database were analyzed to determine how well sample integrity was preserved through the sampling and analytical process, and for accuracy, precision, completeness, representativeness, and comparability, and the results indicated that on the whole the database equals or exceeds the QA/QC expectations of the California State Water Resources Control Board.
5. Where problems were noticed in the database, it was clear that AFWO had discerned the problem early on and had taken corrective actions, and it is also clear that AFWO is continuing to improve the database by adding more QA/QC information to it.
6. AFWO’s Klamath River grab sample database is ready for use in other water quality studies.

6.0 References

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Viescas, John L. 1997. Microsoft Access 97. Microsoft Press, Redmond, Washington.